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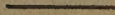
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On the K-Series of the Spectrum of Molybdenum

In consequence of the recent addition to the College of Science of the Three Departments of Zoology, Botany, and Geology and Mineralogy, the present series of the Memoirs of the College of Science will be hereafter entitled "MEMOIRS OF THE COLLEGE OF SCIENCE, SERIES A." and devoted to the papers on mathematics, physics, cosmical physics, geophysics,

The K-Series of the spectrum of molybdenum was investigated by several authors, but some ambiguity still remains for the first lines.

In these experiments the wave lengths of the spectrum were mostly determined by using the spectrum of the first order of the second order.

Papers on zoology, botany, geology, and mineralogy will be published in a new series under the title

The object of the present work is to determine the wave lengths from the spectra of the higher order than the second order. For this purpose a bent mica was used as the crystalline reflector, as its curvature constant is large and its reflecting power is very high.

The bent mica X-ray spectrometer used in this work is the same as that in the former work carried out by O. Yashiki and one of the writers; but some modification has been done on the mode of photographing the spectrum.

Fig. 1 represents diagrammatically the essential features of the experimental arrangement. D is a large lead box with a slit S 0.2mm. wide. O is the center of a wooden cylinder 44.8mm. in radius and on its surface a sheet of mica MN 0.06mm. thick is carefully fastened.

The Editorial Committee.

1127m

On the K-Series of the Spectrum of Molybdenum.

By

Shinsuke Tanaka and Jinzo Tsutsumi.

(With 1 Plate)

(Received April 11, 1923)

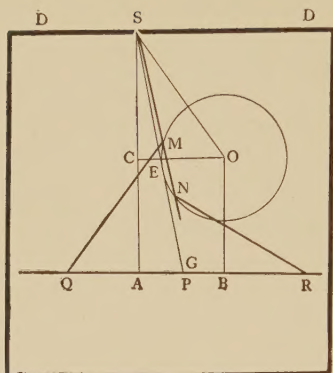
The K-Series of the spectrum of molybdenum was investigated by several authors, but some ambiguity still remains for the faint lines. In these experiments the wave lengths of the prominent lines were mostly determined by using the spectrum of the first or of the second order.

The object of the present work is to determine the wave lengths from the spectra of the higher order than the second. For this purpose a bent mica was employed as the crystalline reflector, as its grating constant is large and its reflecting power is very high.

The bent mica X-ray spectrometer used was essentially the same as that in the former work carried out by U. Yoshida and one of the writers ; but some modification has been done on the mode of photographing the spectrum.

Fig. 1 represents diagrammatically the essential features of the experimental arrangement. D is a large lead box with a slit S 0.2mm. wide. O is the center of a wooden cylinder 44.62mm. in radius and on its surface a sheet of mica MN 0.06mm. thick is carefully fastened.

¹ Yoshida and Tanaka, These Memoirs 5, 173 (1921)



P is a photographic plate.

The source of the X-ray was a coolidge tube with a molybdenum target, whose surface is perpendicular to the axis of the tube, and an induction coil was used to excite this tube. The pencil of rays which leaves the anticathode at a grazing angle is made to pass through the slit S in a slightly divergent form. The ray SM which impinges on the outer surface of the mica at M is partly reflected along MQ to the photographic plate. The part which is not reflected at M penetrates through the mica plate and impinges on the inner surface of the mica at N and here again reflected toward R on the photographic plate.

Let θ be the glancing angle of the ray SM to the cleavage face of the mica at M. If the thickness of the mica is vanishingly small, the glancing angle of reflection at N is approximately equal to θ .

Then the relation between the distance f of the spectral lines appearing on the photographic plate at Q and R and the glancing angle θ of the ray is given by the formula,

$$f = b[\tan(2\theta - \gamma) + \tan(2\theta + \gamma)] + r[\sin(\theta - \gamma)\tan(2\theta - \gamma) - \sin(\theta + \gamma)\tan(2\theta + \gamma)] + 2r\sin\theta\sin\gamma, \dots \dots \dots (1)$$

where b is the perpendicular distance OB from O to the film side of the photographic plate P, r the radius of the cylinder of mica, and γ the angle CSM.

Denoting the perpendicular distance AS from S to the film side of the photographic plate by a , the perpendicular distance OC from O to this line by c , and the length of SO by d and that of SE which is tangent at E on the mica cylinder by e , we have,

$$d^2 = (a - b)^2 + c^2, \quad e^2 = d^2 - r^2. \quad \dots \dots \dots (2)$$

Again let α , β and φ be the angle ASO, ESO and ESM respectively, then

$$\gamma = \alpha - \beta + \varphi. \dots\dots\dots(3)$$

But α , β and φ are given by the following expressions,

$$\left. \begin{aligned} \sin \alpha &= \frac{c}{d} & , & & \sin \beta &= \frac{r}{d} \\ \text{and } \tan \varphi &= \frac{r - r \cos(\theta - \varphi)}{e - r \sin(\theta - \varphi)} & \text{i.e. } \sin \varphi &= \frac{r \sqrt{d^2 - r^2 \cos^2 \theta} - e \cos \theta}{d^2} \end{aligned} \right\} (4)$$

Therefore, when a , b , c and r were known, the value of f corresponding to any value of θ can be calculated from the equation(1).

Hence if we represent the relation between the value of f and θ graphically, the value of θ corresponding to any observed value of f can be readily obtained from the graph. The wave lengths λ for the spectral lines can be calculated from the Bragg's formula $n\lambda = 2d \sin \theta$.

The great advantage of this method lies in the fact that it is not necessary to determine the zero position, i.e. SEG, observation of which often leads to a great inaccuracy.

As the numerical value of d , the grating constant, 9.858°A.U. was taken, the value being that which we have found in the previous experiment by photographing the known wave lengths of the characteristic L-radiation of tungsten. For the value of r , 44.55mm. was taken which is the mean value of the two radii of the inner and the outer surface of the cylindrical mica. This value will introduce the error less than one tenth of a percent to the final result. The actual values of a , b and c in the experiment are as follows :

for the plate No. 1, $a = 169.43 \text{mm.}$ $b = 83.50 \text{mm.}$ $c = 48.96 \text{mm.}$

for the plate No. 2, $a = 208.47 \text{mm.}$ $b = 123.78 \text{mm.}$ $c = 48.75 \text{mm.}$

The calculated value of γ are,

for the plate No. 1, from $2^\circ 53' 37''$ to $3^\circ 20' 11''$

for the plate No. 2, from $2^\circ 45' 17''$ to $3^\circ 11' 51''$

according to the value of θ . (from 1° to 10°)

The photographic plate No. 2 is reproduced in Fig. 2. The time

of exposure was from 20 to 30 hours, the current through the X-ray tube was about 2.5 milliamperes and the potential difference applied was from 40 to 50 kilovolts.

All of the four lines are visible in the third, fourth and fifth orders on the both side, but in the second order the only two prominent lines are visible. The first order lines on the left hand side have been hidden in the dark portion of the photographic plate, and not observable even on the original plate.

In the fourth or the fifth order spectrum some very faint lines seem to be recognized standing close to some of the four lines on the right hand side of the original plate, but their wave lengths could not be determined, because of their absence on the left hand side.

It is here to be added that the higher spectra than the fifth appeared on the right hand side. The intensities of the spectral lines in the different orders show that the odd spectra are more intense than the even ones as is the case in the photographs of the L-series of tungsten in the former experiment.

The values of the wave lengths calculated from the data mentioned above, are tabulated in the table 1. The values obtained by Overn¹, Duane and Patterson² and Leide³ are, for the sake of reference, also given in the table.

In conclusion, the writers wish to express their sincere thanks to Prof. T. Mizuno and Prof. M. Ishino for the interest they have taken in the work.

¹ Phys. R., **12**, 350, (1921)

² Proc. Nat. Acad. Sci. U. S. A. **8**, 85 (1922). and Phys. R., **19**, 542 (1922).

³ Siegbahn, Jahrb. d Radioaktivität u. **18**, 240 (1922).

Table I. Wave lengths in Å. U.

	Order	α_2			α_1			β_1			β_2		
		f_{cm}	θ	λ	f_{cm}	θ	λ	f_{cm}	θ	λ	f_{cm}	θ	λ
Plate No. 1	2	—	—	—	2.410	4°7'17"	0.7085	2.148	3°40'39"	0.6323	—	—	—
	3	3.660	6°13'15"	0.7122	3.635	6°11'0"	0.7078	3.245	5°31'30"	0.6327	3.175	5°24'50"	0.6201
	4	4.596	8°18'50"	0.7127	4.908	8°14'50"	0.7072	4.355	7°21'20"	0.6310	4.268	7°13'0"	0.6192
	5	—	—	—	—	—	—	5.519	9°13'10"	0.6319	—	—	—
	Mean	0.7125			0.7078			0.6320			0.6197		
Plate No. 2	2	—	—	—	3.525	4°6'59"	0.7076	3.145	3°40'29"	0.6318	—	—	—
	3	5.375	6°13'0"	0.7116	5.337	6°10'50"	0.7076	4.745	5°30'50"	0.6312	4.662	5°24'50"	0.6201
	4	7.271	8°18'20"	0.7120	7.207	8°15'0"	0.7073	6.388	7°21'40"	0.6315	6.260	7°13'10"	0.6196
	5	9.250	10°24'25"	0.7123	9.175	10°19'30"	0.7069	8.090	9°11'30"	0.6297	7.936	9°1'30"	0.6186
	Mean	0.7120			0.7074			0.6311			0.6194		
Mean		0.7122			0.7076			0.6316			0.6196		
Overn		0.7129			0.7085			0.6322			0.6212		
Duane & Patterson		0.71213			0.70783			0.63114			0.6198		
Leide		0.71196			0.70759			0.63065			0.61938		

5th

4th

3rd

2nd

1st

2nd

3rd

4th

5th

6th



On the Chemistry of Japanese Plants, II. The Composition of Fossil Wood.

By

Shigeru Komatsu and Hidenosuke Ueda.

(Received May 1, 1923)

There is no need of further discussion now as to the vegetable theory of the origin of coal.¹

The mechanism of its formation from vegetable matter, however, remains to be explained.

The present investigation, therefore, was undertaken to throw some light upon the mode of formation of coal.

K. Yasui² has stated from botanical investigation, that the fossil woods produced near Sendai and Nagoya, belonged to a species of *Sequoia*, and the same opinion regarding the original plant from which "brown lignite"—umoregi,—was formed, was reported by C. Iwasaki in his "A fundamental study of Japanese coal"³—microscopic and X-ray studies on coal.

The specimen of fossil wood from Sendai,—umoregi,—which the authors have examined, was obtained through the kindness of Professor M. Kobayashi of Tohoku Imperial University.

It was dark brown in colour, and the woody structure was perfectly preserved.

The sawdust prepared from the fossil wood, when dried, was readily reduced to powder in a disintegrator. The sawdust freshly prepared from the mass, contained much moisture; the loss in weight

¹ F. W. Clarke: The data of geochem., 1916, 738; W. A. Bone: Coal and its scientific uses, 1919, 23; D. Mendeléeff: The principles of chem., 1905, 1,368.

² Ann. Bot., **31**, 10 (1907).

³ Tech. Reports. Tohoku Imp. Univ., **1**, 109 (1910).

on drying at $98-100^{\circ}$, was 29.2% and that of an air-dried sample was 17.4%.

The air-dried sample was dried on calcium chloride dessicator in vacuo, for 3 weeks (A) and for 5 weeks (B) and was analysed with the following results, calculated on an ash-free, dry basis :

	A.	B.
C.	60.8	61.16
H.	5.9	6.02
S.	0.8	—
Ash.	2.8	2.4

The composition of the ash, obtained on incineration at about 400° in an electric oven, was as follows :

	Komatsu & Ueda.	Iwasaki.
P_2O_5	0.63	—
$S O_3$	35.19	—
SiO_2	20.50	57.31
Fe_2O_3	17.06	8.13
Al_2O_3	18.45	21.13
MnO_2	1.97	—
CaO	23.43	7.69
MgO	1.02	2.21
$Na_2O, K_2O.$	—	3.27

C. Iwasaki¹ has reported the ash-composition of the "brown lignite" (fossil wood) produced near Sendai, as seen in the table.

The results² of the ultimate analysis of wood, peat, lignite, bituminous coal and anthracite, indicate a progressive concentration in the carbon content and a gradual diminution in the oxygen and hydrogen contents. Judging from the ultimate analysis of fossil wood, bearing in mind that the successive transformation from wood to anthracite was

¹ Loc. cit.

² W. A. Bone: *Coal and its scientific uses*. 50; C. F. Cross and E. I. Bevan: *Cellulose*, 1910, 239.

attained with some numerical relations in the composition, this fossil wood seems to represent an intermediate stage like peat between wood and lignite in the formation of coal.

	C.	H.	O.	N.
wood	49-51	6.2-6.3	42-45	0.5 -0.9
peat	50-64	4.5-6.8	28-48	0.30-7.5
lignite	60-75	5.0-5.2	20-35	0.75-1.75
bituminous coal	75-90	4.5-5.5	5-15	0.75-1.75
anthracite	90-95	2.5-2.8	2.7-3.0	0.5 -1.0

As seen in the foregoing table, the ash of fossil wood contains more sulphur and less nitrogen compared with that of coal. When a plant died, the processes of decay and destruction followed; the wood, instead of being left in the open air, was buried under successive layers, either of matter like itself or else of sediments such as clay under those conditions, the action of oxygen was retarded, and the formation of earth molds was aided, i. e. incomplete oxydation of plant tissues took place, and the degradation products of plant tissues succeeded the accumulation of carbon at the expence of oxygen and hydrogen by a gradually increasing pressure and the heat generated thereby.

To find some chemical changes which took place in the constituents of wood buried under earth, the content and nature of resinous matter, carbohydrates and lignin in fossil wood were studied.

1. RESINOUS CONSTITUENT.

250 gramm. air-dried sample (17.4% water) were treated with 91% alcohol in hot state, and the extract filtered from the insoluble matter was evaporated under reduced pressure and the residue heated in a steam bath to constant. This dried residue weighed 10.6 gramm., which corresponded to 5.3% of the dried sample.

In another experiment, 150 gramm. of the sample yielded 7 gramm. resinous matter (5.6% the sample).

The resin thus obtained, was a brown amorphous substance, possessed an aromatic odour, yielding by potash fusion a phenolic compound and an acid of butyric acid odour, and the former showed bluish green coloration with ferric chloride and formed with bromine water yellow precipitate from its alcoholic solution.

The methoxy value was 0.84% measured by Zeisel's method, and the elementary composition of the resin was as follows :

C.	74.29 ;	73.72 ;	73.57	mean	73.81
H.	6.89 ;	6.60 ;	6.47	„	6.65
Ash.	1.66 ;	1.56 ;	1.41	„	1.54

The above mentioned analytical results of the isolated resin mass, calculated on an ash-free, dry basis, agree with those of the resinous constituents found in coal investigated by White¹.

2. CARBOHYDRATES.

A dried sample was heated with 1% HCl in a sealed-tube at 137–144° for 6 hours, and the acid-extract separated from the insoluble matter. The content of simple sugar was determined by means of Fehling's solution : it amounted to 5.1% of the sample, calculated as d-glucose.

Pentosans (furfural yielding compounds) in the sample estimated by the Tollens and Kruger-method².

The phloroglucide, thus formed, was observed to be composed entirely of methyl furfural phloroglucide, by the spectroscopic investigation of $N/10000$ alcoholic solution.

The cellulose-content and the preparation of a pure sample of cellulose from the fossil wood, were studied by the method first tried by Cross and Bevan and then modified by Renker.³ The purified sample was white in colour, contained no substance yielding methyl iodide by treating with hydrogen iodide solution, and gave the following results

¹ Bone: Coal and its scientific uses, 19.

² Z. angew. Chem. 40 (1896).

³ J. Soc., Chem. Ind., 28, 1269 (1910).

on analysis, taking it to be an ash-free, and dry substance.

$$C=44.01, \quad H=6.19, \quad \text{ash}=0.65.$$

(Theory required for $(C_6H_{10}O_5)_n$; $C=44.44$; $H=6.17$). It was also confirmed to consist of pure cellulose, yielding by acid hydrolysis d-glucose.

3. LIGNIN.

Its content in the sample was estimated by following Ost & Wilkennig and J. König¹. It was treated with 72% sulphuric acid and water, alcohol and ether successively, and the lignin-content was calculated from the loss of weight, taking the average of two experiments. The residue was analysed and the following results were obtained, the sample being taken as an ash-free, dry substance.

$$C=64.06; \quad 63.86; \quad H=5.52; \quad 5.54$$

$$\text{Ash}=0.5; \quad 0.9; \quad CH_3O=3.85$$

Lignin-content, on the other hand, in the sample, calculated indirectly from its methoxy value determined by the method of Benedikt and Bamberger² was 56.5% being 2.989 methoxy value. The methoxy value of the sample, the resinous matter having been removed by treating with alcohol, was 3.145 and consequently 59.43% was assigned for lignin-content.

The approximate analysis of the fossil wood calculated as ash-free, dried substance was as follows :-

	Water.	Ash.	Resin.	Methyl Pentosan.	Total Polysaccharide.	Lignin	Cellulose.	Total.
1.	17.18	0.994	6.09	1.87	5.44	56.50	30.07	—
2.	17.61	1.064	5.59	1.66	4.81	55.88	30.90	—
3.	—	—	5.98	—	—	—	28.30	—
Mean	17.40	1.03	5.88	1.77	5.13	56.19	29.36	96.57

On comparing the analytical results above mentioned with those

¹ Chem. Zeitung, **52**. 461 (1910); Chem. u. Struktur d. Pflanzen-Zell., 1914, 50.

² Monat Chem., **11**. 260 (1890).

of red wood¹ (*Sequoia Sempervirens*) (A) and also of other coniferous woods (B) compiled from many analysis², disregarding the ash and water content, we have learned that in our plant by keeping under the ground, 20% cellulose, 4% other polysaccharides were destroyed, on the other hand 25% of lignin and 2% of resinous matter, were accumulated.

	(A)	(B)
Resin and fat	4.5	3
Lignin	30.2	30
Carbohydrate	8.6	10
Cellulose	52.0	50

The content of cellulose and other polysaccharides in a peat buried at 20-100 cm. below the surface, studied by H.V. Feiltzen and B. Tollens,³ being 15.20% and 12.75% respectively, shows fair agreement with our results, both fossil wood and peat being regarded as having the same relationship in the formation of coal, judging from their ultimate analysis.

Cellulose and other polysaccharides composed of plant cell-wall, and nitrogenous matter found in cell-sap are less resistant to attack of organisms and these compounds should be decomposed by organisms into methane, CO₂, water and other simple substances. On the contrary, resinous matter is most resistant to bacterial decay.⁴

This opinion harmonizes with the investigations by Katayama⁵ and others⁶ on the natural decay of pine and oak by organisms. Some of the carbohydrates and nitrogenous substances in wood were naturally destroyed in this way and the remainder would suffer incomplete oxidation or dehydration caused by pressure or heat under the earth crust, and consequently the compounds with open carbon chains which are

¹ W. H. Dore: J. Ind. Eng. Chem., **11**, 558 (1919).

² Cross and Bevan: p. 177; G. Scowalbe: p. 441; J. V. Wiesner, D. Rohstoffe Pflanzenreiches, II. 332 (1918).

³ Ber. D. Chem. Ges., **30**, 2571 (1897).

⁴ F. Tideswell, and R. V. Wheeler: J. Chem. Soc., **121**, 23 (1922); Clarke, p. 740, 763.

⁵ Kogyo Kwagaku Zashi, **17**, 611 (1914).

⁶ Cross and Bevan: 1910, 239.

permitted to maintain and manifest life in plants were transformed into substances of cyclic structure without nutritive value by losing these faculties¹.

Thus, all of the organic substances in plants their open carbon chains being closed within their molecule, forming carbon rings, enter their stabler state, or state of repose, their activity disappearing, and "la cyclisation est la mort"² is our working hypothesis in the present study.

Feb. 1923. Laboratory of Organic and Biochemistry.

¹ A. Pictet; *La structure moléculaire et la vie*, 1915. p. 10.

² A. Pictet. *Loc. cit.*

On Kakishibu, I. Constitution of Shibuol,* I.

By

Shigeru Komatsu and Naohiko Matsunami.

(Received May 2, 1923)

Kakishibu, in Japan, is prepared by treating unripe Kaki fruit of the astringent variety, crushed in a fresh state, with water at ordinary temperature and separating insoluble pulp from the extract¹.

It is used for the preservation of fish nets and fish lines, and wooden vessels and also to make paper water proof. Such technical applications of kakishibu, may be attributed to its containing a tannin-like substance in it.

The freshly prepared kakishibu is a light yellow turbid solution, and on standing in the open air, it turns gradually from yellowish brown to dark brown, by oxidation of the phenolic compound and forms a film on the surface of the solution.

The specimen used in the investigation was prepared on the 14th of Sept. 1922, specially from "AWASO", the astringent variety, grown at Seta, Shigaken, and started the experiments on the 26th of Oct. 1922.

It was a brownish-yellow turbid solution, sp. gr. 1.02. After many trials, the authors succeeded in getting a clear and transparent solution, by filtering through an asbestos mat in Buchner's funnel, using suction as usual.

The solution becomes light reddish-brown, by such treatment. It gives with ferric chloride solution, a bluish black precipitate which treated with dilute hydrochloric acid solution, changes into white. With

* The expenses of this investigation were shared by the Department of Education.

¹ Tsukamoto; Bull. Coll. Agri. Tokyo. 4. 329 (1902).

bromine water, a pale yellow precipitate was formed which indicates a phenolic compound presents in the solution.

This assumption was confirmed by preparing an azo-compound by coupling with diazobenzenechloride. The authors, therefore, chose the name "SHIBUOL" for the phenolic compound supposed to exist as a constituent of kakishibu.

Shibuol was precipitated as a lead salt from the solution, with both basic and neutral lead acetate solutions. This precipitate is soluble in dilute acetic acid. It formed a white amorphous compound with formaldehyde and a little dilute hydrochloric acid.

Shibuol was also precipitated as noticed by Tsukamoto¹, in a white amorphous compound which changed gradually to brown by treating with mineral and also acetic acids in a cold state. When treated with conc. sulphuric acid, it yielded a light yellow amorphous precipitate, which dissolved in the solution when gently warmed, and on boiling further a red-coloured amorphous precipitate, similar to "phlobaphene" was reproduced.

So far as we could ascertain, shibuol should be classified as phlobatannin².

Although many chemists³ have attempted to determine the constitution of shibuol, even isolation of the constituents has not yet been achieved owing to the difficulty of obtaining shibuol, in an even approximately pure state from kakishibu.

The authors, however, have succeeded in isolating shibuol in fairly pure condition from kakishibu, in the following ways:—

¹ Loc. cit.

² S. Komatsu and H. Ueda: *J. Biochem.*, **2**, 298 (1923).

³ Tsukamoto: *Loc. Cit* 29; W. D. Bigelow, H. C. Gore and B. T. Howard: *J. Am. Chem. Soc.*, **28**, 688 (1906); F. E. Lloyd: *Biochem. Bull.*, **1**, 7 (1911); D. E. Clark: *Ibid.*, **2**, 412 (1912).

I. ISOLATION OF SHIBUOL.

1. BY PRECIPITATION WITH A MIXTURE OF ALCOHOL AND ETHER.

1000 c.c. of kakishibu prepared in clear and transparent state by filtration, were evaporated under reduced pressure to syrup, and treated with a mixture of alcohol and ether to precipitate shibuol. It was separated by filtration from the mother liquor, and washed with water, alcohol and ether successively, yielding 20 grms, corresponding to 2% of the kakishibu.

2. BY PRECIPITATION WITH GLACIAL ACETIC ACID.

2000 c.c. of the clarified shibu were evaporated under reduced pressure to a syrup, and treated with glacial acetic acid in a cold state. The precipitate, thus formed, was soluble in water. On being kept in contact with the acidic solution for a few hours at an ordinary temperature, it became insoluble. This insoluble substance was then washed with water, alcohol and ether. The sample, dried at 50° in vacuo, weighed 28 gm. (1.4% of the solution).

3. BY PRECIPITATION WITH CONC. HYDROCHLORIC ACID.

2000 c.c. of the kakishibu, evaporated to a syrup under reduced pressure as usual, were treated with cold conc. hydrochloric acid, and the precipitate formed, separated from the mother liquor, was washed with water, alcohol and ether, and dried at 50° in vacuo, yielding 21 gm. shibuol (1.2 %).

4. BY PRECIPITATION WITH BASIC LEAD ACETATE SOLUTION.

1000 c.c. of the clarified kakishibu, were treated with a sufficient quantity of basic lead acetate solution to precipitate completely the shibuol. The insoluble lead salt, separated from the mother liquor, was washed with water. It was suspended in 500

c.c. water, and was decomposed by passing sulphuretted hydrogen gas over it. The filtrate, separated from lead sulphide, was light yellow. It was evaporated under reduced pressure almost to dryness, treated with 98% alcohol to precipitate shibuol, and filtered, washed with ether, and then dried in vacuo. It yielded 10.6 grm. (1% of the kakishibu).

The shibuol, when freshly isolated from the kakishibu by precipitation methods, was soluble in water. On standing in contact with the mother liquor for a few hours, however, it changed to the insoluble form. The shibuol thus obtained was soluble in alkali, but insoluble in water, alcohol, acetone and acetic ester.

It was dried at 100° under reduced pressure to constant weight, and analysed with the following results, calculated as ash free substance.

TABLE I.

Samples.	Carbon.			Hydrogen.			Ash. mean
	1.	2.	mean	1.	2.	mean	
Prepared with							
1. alcohol and ether.	56.84	56.67	56.76	4.45	4.36	4.41	1.96
2. hydrochloric acid.	56.67	56.35	56.51	4.04	3.96	4.00	0.28
3. glacial acetic acid.	56.26	—	56.26	4.26	—	4.26	0.28
4. basic lead acetate.	56.61	56.33	56.47	3.76	3.72	3.74	0.15
Mean value.			56.5			4.1	

It contains no reducing sugar, and yields by digesting with zinc-dust and water, gallic acid and phloroglucinol as observed in maletto tannin occurs in the bark of *Eucalyptus occidentalis*¹.

II. CONSTITUENTS OF SHIBUOL.

Studies of the well marked reactions of shibuol mentioned above, and of the colour reactions² of the hydrolytic products of the "tannin-masses" from the fully ripe fruit of the persimmon, by treating with

¹ F. Czapek; Biochem. Pflanzen. III, 498 (1921); A. G. Perkin and A. E. Everest; The natur. organ. colour. matters, 443.

² E. D. Clark; Loc. cit.

dilute mineral acids or alkali, led the authors to the conclusion that the chief constituents of shibuol, formed by hydrolysis, should be phloroglucinol and gallic acid.

Shibuol was, therefore, subjected to alkali-fusion to ascertain the above idea by isolating these compounds from the reaction products.

(1) FUSION WITH ALKALI.

5 grms. shibuol prepared by the second method, were digested in a silver dish with 15 gm. caustic potash and 5 c.c. water, until the mixture became pasty. The fused mass was dissolved in 200 c.c. water, and acidified with dilute sulphuric acid, whereas a brown amorphous precipitate (A) was formed, and filtered. The filtrate was evaporated to dryness (mass B) under reduced pressure.

The dark brown mass (B) was treated with a mixture of 140 c.c. 94 % alcohol and 210 c.c. ether in Sudo-Kumagawa's apparatus for 6 hours to extract phloroglucinol and gallic acid formed by hydrolysis.

The extract was subjected to distillation to get off the solvent, and the residue dissolved in 200 c.c. water. To separate gallic acid from phloroglucinol, the aqueous solution was treated with neutral lead acetate solution to precipitate gallic acid only as an insoluble lead salt (C), and filtered. The precipitate (C) was washed with water, suspended in water and decomposed by means of sulphuretted hydrogen.

The aqueous solution containing gallic acid, was separated from lead sulphide, and concentrated under reduced pressure, and gallic acid was crystallised in needle form thereby. It melted at 239–240°. The yield was 0.08 gm.

The filtrate containing soluble lead salt, separated from precipitate (C), was also treated with sulphuretted hydrogen gas to get phloroglucinol in a free state. The solution, separated from lead sulphide, was evaporated under reduced pressure. Phloroglucinol amounting to 0.2 gm., was obtained in a crystalline state. It melted at 209–211°.

Two specimens obtained in a pure crystalline state, were identified to be gallic acid and phloroglucinol respectively, by studying the colour reactions towards ferric chloride and also by determination of their melting points.

The substance supposed to be gallic acid was dried at 100° in vacuo for 5 hours, and was analysed with the results : C=49.36 ; 49.42; H=3.57 ; 3.65 (theory requires C=49.41 ; H=3.52 for $C_6H_2(OH)_3COOH$).

Phloroglucinol, obtained from shibuol, was analysed after being dried at 60° in vacuo for 5 hours : C=56.88 ; 56.34 ; H=4.50 ; 4.80 (theory requires C=57.14 ; H=4.76 for $C_6H_3(OH)_3$).

(2) PHLOROGILUCINOL-CONTENT IN SHIBUOL.

This was estimated approximately by following E. Vrotoček and R. Potmešil's directions¹ which were used in the estimation of phloroglucinol in phloretin, apigenin etc.

Phloroglucinol formed by potash-fusion, was precipitated with furfuraldehyde in hydrochloric acid solution. It was expected the yield of furfurolphloroglucide will be effected by the formation of an insoluble mass after the fused solution was acidified.

0.436 gram. Shibuol prepared by the third method, were digested with 7 gram. caustic potash and 2.5 c.c. water, acidified with 34.8 c.c. conc. hydrochloric acid and made up to 100 c.c. Phloroglucinol formed in the solution, was precipitated as furfurolphloroglucide, which was filtered after 24 hours on Gooch's crucible, washed, and dried at 105° in an atmosphere of hydrogen gas.

The amount of phloroglucinol was calculated from the phloroglucide (weighing 0.3258 gram.), to be 49.7 %.

The phloroglucinol content in other samples, was also determined, and the results were as shown in the table II.

¹ Ber. D. Chem. Ges., **49**, 1185 (1916).

² Monat. Chem., **6**, 989 (1885).

(3) METHOXY VALUE OF SHIBUOL.

It was estimated by following the Zeisel direction² as usual and the results were as shown in the table II.

TABLE II.

Samples.	Methoxy Valuc.		Phlorogluciol.
1. Prepared with alcohol and ether.	0.18	0.23	49.12
2. „ „ hydrochloric acid.	0.85	—	49.71
3. „ „ glacial acetic acid.	0.27	—	42.86
4. „ „ basic lead acetate.	0.46	—	39.67

(4) THE INSOLUBLE SUBSTANCE (A)

It was a brown amorphous substance soluble in alkali. The carbon and hydrogen content in the sample and also the methoxy group were determined with the following results :

C.	61.70 ;	61.72	mean.	61.71
H.	3.10 ;	3.29	„	3.20
CH ₃ O.				1.57

It contains more carbon and less hydrogen as compared with shibuol.

A comparison of the ultimate analysis, indicates much resemblance with the brown substance named "goma," found in the pulp of ripe fruit of the sweet variety and also of the dessicated fruit.

III. KAKI-GOMA.**(1) ISOLATION OF KAKI-GOMA.**

It was a brown amorphous substance formed naturally in the fruit of the sweet variety, and also found in the dessicated fruit of the astringent one¹.

The kaki-goma used in this investigation was isolated in the following ways from the pulp of the dessicated fruit named dojo-hatiya, produced at Ogaki, Gifuken.

¹ S. Komatsu and Ueda : Loc. cit.,

(a). The pulp was digested with water to remove soluble matter such as simple sugars and pectin and then treated with 72 % sulphuric acid to dissolve cellulose remaining with goma in the pulp, and washed again with boiling water.

20 gramm. of crude goma thus prepared, were treated with 100 c.c. of 10 % acetic acid, washed with water, and shaken with 72 % sulphuric acid in a flask for 3 hours and finally washed with water to remove the acid completely. The yield of goma was 6.3 gramm.

To purify the crude goma, 34 gramm. of the sample, were treated with 300 c.c. hot alcohol, washed repeatedly with water, and dried.

The dried substance was sifted with a 50 mesh-sieve, and yielded 9.3 gramm. pure goma.

(b). It was treated with 100 c.c. 72 % sulphuric acid for 5 hours, and the soluble matter washed off. Some impurities associated with the goma can easily be removed mechanically by decantation from the goma, which sinks to the bottom of the vessel. On the process being repeated, fairly pure goma was obtained. The yield was 8 gramm.

It was soluble in alkali, but insoluble in all organic solvents, and gave the following results on analysis after being dried at 130° for 3 hours :

C.	59.90 ;	59.83	mean	59.87
H.	3.84 ;	3.67	,,	3.76
CH ₃ O.				1.94
Phloroglucinol.				17.88

(2) POTASH FUSION OF KAKIGOMA.

6.3 gramm. kaki-goma were digested with 20 gramm. caustic potash and 7 c.c. water in a silver dish. The fused mass was dissolved in 150 c.c. of water, and acidified with sulphuric acid, whereupon a dark brown precipitate was formed, which was separated by filtration, and washed with hot water.

The combined solution of filtrate and washings, was evaporated as usual under reduced pressure, and the phenolic compounds extracted with a mixture of alcohol and ether. The residue remaining after the solvent had been evaporated off, was dissolved in water, and treated with neutral lead acetate.

The insoluble lead salt, thus formed, was confirmed to be a salt of gallic acid, the free acid being isolated by the usual processes (m. p. 239—240°). The yield was 0.15 gm.

From the filtrate containing soluble lead salt, however, a trace of a substance, was obtained giving the same colour reaction as phloroglucinol towards ferric chloride.

In the same manner, using 3.5 gm. pure goma, we obtained after hydrolysis 1.8 gm. of a dark brown substance, insoluble in an acidic solution.

It was dried at 130° in an air-bath for 3 hours, and analysed with the following results :

C.	62.99 ;	62.78 ;	mean	62.88
H.	3.74 ;	3.75 ;	„	3.74

It is anticipated that the transformation of shibuol by hydrolysis into a brown substance will be shown to have some connection with the formative of kakigoma in the fruit, in course of ripening, and the relation between kaki-goma and phlobaphene will be discussed in a succeeding article.

Summary.

1. The shibuol isolated by the precipitation methods, on analysis gave numbers expressed by the empirical formula $C_{14} H_{20} O_9$.
2. Shibuol, on fusion with potash, gave a substance represented by the formula, $C_{12} H_8 O_5$, and phloroglucinol and gallic acid.
3. Kakigoma of the empirical formula, $C_{11} H_9 O_5$, by potash fusion, yielded some phloroglucinol and a large yield of gallic acid and a substance represented by the formula, $C_{13} H_9 O_5$.

April. 1923. Laboratory of Organic and Biochemistry.

Constitution of Polysaccharides, II.

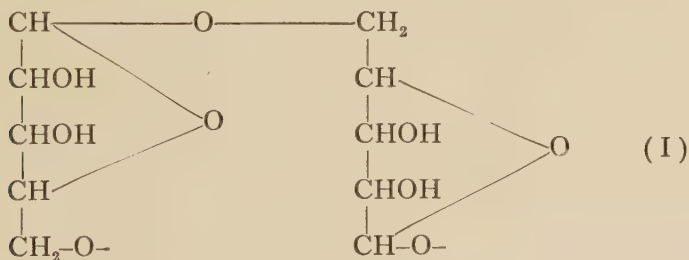
Constitution of Xylan.

By

Shigeru Komatsu, Tetsuji Inoue and Risaburo Nakai.

(Received May 1, 1923)

In the previous article on this subject, S. Komatsu and K. Kashima¹ proposed the constitutional formula (I) for xylan prepared from wheat straw, based on acetylation, yielding mono- and di- acetyl compounds. With regard to the exact position of the two free hydroxyl groups in the constituent pentose, study of the chemical dynamics of the hydrolysis of xylan and its acetyl derivatives seems to afford no evidence, and remained to be solved.



Among many devices, the investigations of the methylated sugars proposed by J. C. Irvine and W. N. Haworth² has been recognised by chemists as bringing the most satisfactory results in this problem.

The present study was, therefore, concerned with the preparation of methyloxylan, its hydrolysis and the oxidation of the cleavage product.

1. XYLAN.

Xylan was prepared from two sources, one wheat straw, and the other rice straw, both grown in Kyoto. The procedure used in the

¹ These memoirs, 5, 313 (1922).

² J. Chem. Soc., 109, 1321 (1916); 115, 593, 809 (1919).

preparation was the same as that described in the previous article,¹ and the yield of the crude xylan was 14% in the former and 19% in the latter. When calculated on samples, purified by repeating the precipitation and treatment with hydrochloric acid, the yield was reduced to 6.6% and 8.2% respectively. 210 grm. of air dried wheat straw yielded, by Salkowski's¹ method, 4 grm. pure xylan. The purified samples, on analysis, gave the following results, calculated as ash free substance.

1. Xylan from wheat straw :

	C=45.00	H=6.33	Ash=0.66
	45.14	6.16	0.84
	45.40	6.00	0.76
	45.30	6.21	0.86
	45.34	6.21	0.75
mean	45.23	6.18	0.77

2. Xylan from rice straw :

	C=44.78	H=6.10	Ash=1.45
	45.26	6.03	1.68
	45.06	6.11	1.48
mean	45.03	6.08	1.54

3. Xylan from wheat straw by Salkowski's method.

	C=45.53	H=6.01	Aas=4.60
	45.66	5.20	5.03

The specific rotatory power of xylan from rice straw in 2.5% caustic soda solution, showed $[\alpha]_D^{20} = \frac{-4 \times 100}{0.046 \times 100} = -14.49$.

2. DIMETHYL ETHER OF XYLAN.

Methylation of Xylan by the method of Pudie and Irvine,² with the silver oxide-methyl iodide reaction, was tried but with no result. While the authors were engaged in the methylation, E. Heuser and W. Ruppel's article³ "Über Methyläther des Xylans" appeared. The

¹ Zs. Physiol. Chem., **34**, 162 (1901).

² J. Chem. Soc., **83**, 1021 (1903); **85**, 1049 (1904)

³ Ber. D. Chem. Ges., **55**, 2084 (1922).

method used in the preparation of methyloxylan was similar to their processes, somewhat different in details.

10 gram. xylan from wheat straw were treated with 150 c.c. 30% sodium hydroxide solution and 100 gram. dimethylsulphate, and the methyloxylan deposited on heating with some water, was separated by filtration from the mother liquor. The crude product was washed with hot water to remove some inorganic substance admixed, and dried in a dessiccator; it was 6.5 gram. 35 gram. of xylan from rice straw, in the same way, yielded 32.5 gram. crude methylated compound which consisted of partly and fully methylated derivatives as described by Heuser and Ruppel. It was, therefore, soon methylated completely by treatment with silver oxide and methyl iodide in the following manner: 1 gram. raw methyloxylan, 6 gram. silver oxide and 20 gram. methyl iodide were heated in a sealed tube at 100° for 3 days, and the product, separated from silver salt, on distilling off the volatile substance, gave a syrup. It was extracted with chloroform in Soxlet's apparatus, and on the solvent being evaporated there remained a light brown syrup, which after drying for 3 weeks in vacuo at 80°, became solid softening at 50-60°.

It gave, on analysis, the following results:

C=52.61; 52.31; H=7.70; 7.37; CH₃O=35.77; 36.19., theory requires C=52.47; H=7.56; CH₃O=38.76 for C₅H₆O₂(OCH₃)₂.

The specific rotatory power of the substance in chloroform solution, $[\alpha]_D^{20} = + \frac{37' \times 10}{0.2025 \times 60} = + 30'.45$, showed an opposite sign to that acetyl derivatives of xylan.

3. HYDROLYSIS OF DIMETHYL XYLAN.

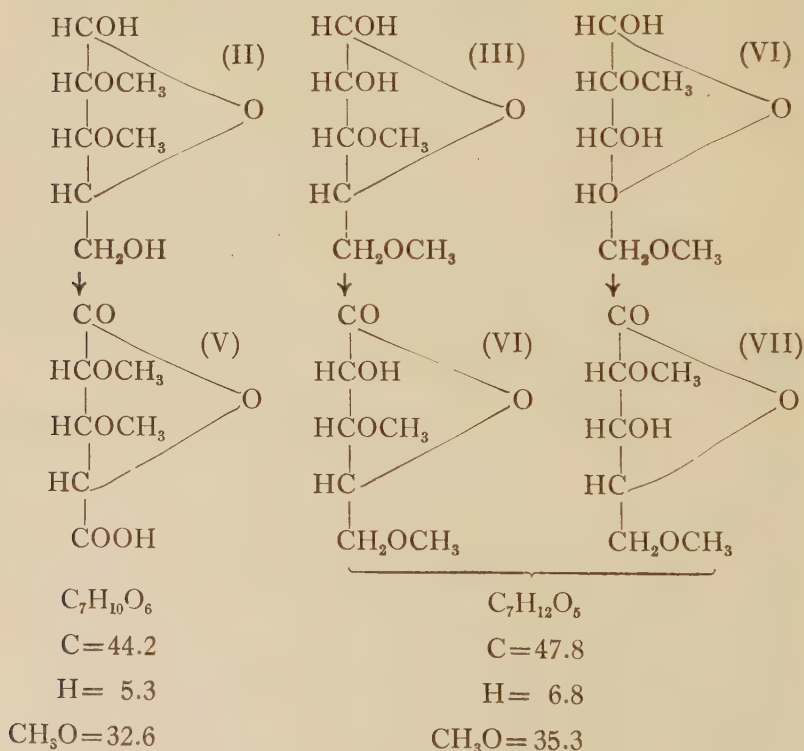
2 gram. dimethyl ether of rice xylan were heated in 200 c.c. 5% HCl solution (sp. gr. 1.024) at 100° for 4 hours. When hydrolysis was complete, the acid solution was neutralized by treating with freshly precipitated silver carbonate, filtered, and heated at 50° with some charcoal and again filtered.

To remove trace of silver salt in the solution, it was treated with

sulphuretted hydrogen, and filtered, and the filtrate was evaporated to syrup at 40° under reduced pressure. The remaining syrup consisted of dimethyl xylose, which reduced the Fehling solution, but not potassium permanganate solution. It was soon subjected to oxidation without isolating the sugar in the pure state.

4. OXIDATION OF DIMETHYL XYLOSE.

Three constitutional formulae of the butylene oxide type are possible for dimethyl xylose, the cleavage product from the hydrolysis of dimethyl xylan :



The two free hydroxyl groups in these formulae must have been precisely those groups concerned in the coupling of the pentose in the original xylan, since all the hydroxyl groups exposed in xylan are protected by a methyl group in dimethyl derivative.

Methyl xylose, thus formed, when oxidized carefully with nitric acid as in the cases of methyl hexoses observed by Haworth¹, should be transformed into a methylated sugar acid as shown in the scheme. Of these possible formulae, (III) and (IV) can easily be excluded by finding the proof for the presence of a free primary alcohol group in the isolated pentose.

Granting formula (II) for the methyl xylose, a lactonic acid having the molecular formula $C_7H_{10}O_6$ (V) and containing two methoxy groups, should result from its oxidation.

The syrup obtained by hydrolysis of methyloxylan, was oxidized with 20 c.c. nitric acid ($D=1.2$) following precisely Haworth's direction². The reaction temperature was maintained at 80° for a few minutes, and thereafter at 65° for $3\frac{1}{2}$ hours. The acidic solution was treated with alcohol and then ether and afterwards evaporated under reduced pressure, to remove completely nitric acid, and finally a pale bluish white syrup was obtained which was dried at 80° under reduced pressure for many weeks. The yield of the oxidation product was 0.8 gm. It gave, on analysis, the following results :

C=45.06 ; H=5.49 ; $CH_3O=28.23$.

(Theory requires C=44.2 ; H=5.3 ; $CH_3O=32.6$ for $C_5H_4O_4(OCH_3)_2$).

The results agree with the theoretical value for optically active dimethoxy glutaric acid (V). The specific rotatory power of the acid in alcohol solution showed $[\alpha]_D = \frac{+1.82 \times 100}{0.0137 \times 100} = +132^\circ$.

Admitting that the fully methylated xylan gives, when hydrolysed with dilute acid, methylated simple sugar, in which the linkings are preserved exactly as in the parent polysaccharide, and tracing it back reaction by reaction, the authors are led to conclusion that the constitu-

¹ Loc. cit.

² J. Chem. Soc., 115, 815 (1919).

30 S. Komatsu, T. Inoue and R. Nakai. *Constitution of Polysaccharide, II.*
tional formula for xylan is as represented in formula(I).

The authors wish to thank Dr. B. Masumoto for his help on analysis of the lactonic acid and its optical measurement.

April 1923. Laboratory of Organic and Biochemistry.

Use of Zinc Amalgam in the Evolution Method for Determination of Sulphur in Iron and Steel.

By

Teruo Ashida.

(Received May 21, 1923)

The evolution method as a way of determining sulphur in iron and steel is much appreciated in technical practice by reason of its being simple and much quicker than the gravimetric (barium sulphate) method. Reproaches have, however, been often raised against the unreliability of the process, which is said to give too low percentages for sulphur. It is true that the process has defects in its fundamental principles, inasmuch as the states of sulphur in iron and steel are varied and so not necessarily destined to give hydrogen sulphide on being treated with hydrochloric acid. In fact, some might remain unaffected, some be changed into organic sulphides. Furthermore, a solution of hydrogen sulphide is liable to be oxidised into sulphuric acid on coming into contact with oxygen kept in solution or in the air. It may also liberate sulphur on being brought into reaction with ferric chloride in solution. In spite of such differences of conditions, we are usually in the habit of using this method with no care for any of them, and this must be one reason why the results lack accuracy.

We shall now see, therefore, what would be the real states of sulphur in iron and steel and consider the best means to meet them as well as other difficulties associated with the method.

Sulphur combines with iron to form the sulphide, which may exist either in isolated crystals uniformly distributed or segregated from it, or in a solid solution, which is likely to be the case when the molten metal is too rapidly cooled. Under such different states of existence, the action of hydrochloric acid can never be the same. First of all, if the acid is dilute, the rate of evolution¹ of hydrogen sulphide must be slow and lead to its easier oxidation, whereas the formation of organic sulphides would be much greater. If, on the contrary, the acid be stronger, the rate of evolution will be greater and naturally prevent oxidation of hydrogen sulphide. Yet even in that case, we might suspect some of the sulphur in solid solution would not be converted into hydrogen sulphide but be separated rather as free sulphur. As a remedy for the latter difficulties, it has been the habit to anneal the material before it is subject to analysis. A similar instance perhaps may occur, too, after the effects of ageing upon steel. These effects are indeed nothing but the oxidation of samples and must tend to keep the sulphur partly as sulphates and partly in the free state. They would, therefore, be cancelled, as is generally known, by reheating the materials with carbon at high temperatures. However effective be each of the pre-treatments, so far as they are not unified, the evolution method would be a little too troublesome. Moreover, the use of too strong acid can not be held as convenient on several grounds.² We shall now remark, too, that the Bureau of Standards, U. S. A., is also of opinion, that the results of the evolution method are too low, the data for which are to be given later on.

According to my experience, all these difficulties can, however, easily be overcome by making use of the stronger acid, sp. gr. 1.15–1.10, in presence of zinc amalgam. Vivid evolution of hydrogen will on the

¹ For the influence of the rate of evolution on the production of hydrogen sulphide, see Matthewman: *West of Scotland Iron and Steel Institute*, Session 1896-97.

² Bauer and Deiss, *Analyse von Eisen und Stahl*, 2nd. Ed., p. 210,

one hand keep hydrogen sulphide from oxidation, and on the other reduce the liberated sulphur or sulphuric acid into hydrogen sulphide, whereas the formation of organic sulphides would mostly be prevented thereby. The use of tin and hydrochloric acid as recommended by Treadwell³ cannot excel my process, because we have in our case not only a steady vivid evolution of hydrogen but also mercury reduced serving as a catalyser for the intended reactions.

As to the concentration of the acid, in so much as there is zinc amalgam in addition to the samples, it is obvious that we want more of it, so that we may use it in a concentrated state in order not to have the liquid in the gas generator too bulky. Fumes from such a stronger acid can easily be caught by placing a wash-bottle next to the generator. The following is a full description of my modification.

REAGENTS.

1. Hydrochloric acid : sp. gr. 1.20.
2. Zinc amalgam : about 8 gr. pure crystallised mercuric chloride mixed with about 1/2 kg. pure zinc in grains of 2–3 mm. sizes, covered with water, shaken till the reaction is over, well washed with dilute hydrochloric acid and then with water, and finally dried.
3. Ammoniacal solution of cadmium chloride : 120 gr. cadmium chloride dissolved in 1500 c.c. water, to which 600 c.c. conc. ammonia is added.
4. Iodine solution : 2.539 gr. resublimed iodine mixed with 5 gr. potassium iodide, dissolved in 100 c.c. water and made up exactly to 1000 c.c.
5. Thiosulphate solution : about 5 gr. crystallised sodium thiosulphate dissolved in 1000 c.c. water and titrated exactly against the iodine solution.

³ Ber. XXV, 2377.

ARRANGEMENT.

The arrangement is as shown in the following figure:—

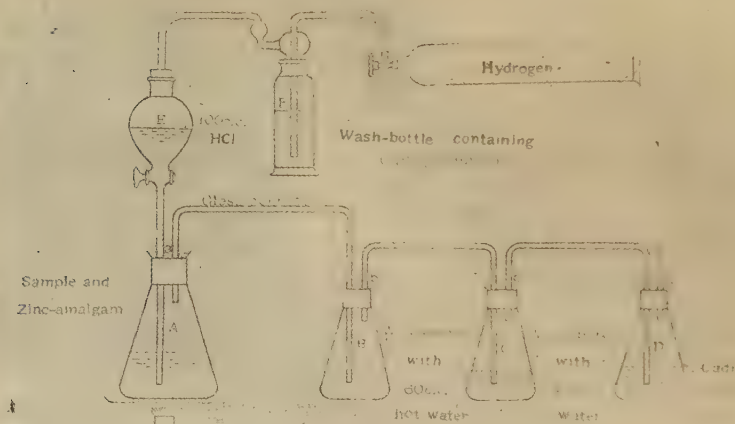


Fig. 1.

A: Hydrogen sulphide generator with a glass-stopper *a*, of which the upper side is covered with water.

E: Drop-funnel inserted into the generator A through the glass-stopper, its upper mouth being connected with a hydrogen reservoir.

B: Wash-bottle containing hot water in order not to keep hydrogen sulphide but to be able to catch as much hydrochloric acid gas as possible. Glass-connection for this and generator. Water jacket at *b*.

C: Wash-bottle. Hydrogen sulphide in this bottle, if any, must be measured and added to the main part in the next bottle. Water jacket at *c*.

D: Hydrogen sulphide absorber, which contains 10 c.c. standard cadmium solution diluted with 50 c.c. water. Water jacket at *d*.

PROCEDURE.

Two or three gr. of a sample crushed in pieces or in turnings and about 10 gr. of zinc amalgam are weighed into the generator A and well mixed by shaking, and the acid is then poured in from the drop-funnel. As soon as the reaction has begun to die down, a hydrogen stream is allowed to pass, which will first force in the remainder of the acid and then fill up the bottle so as to keep it air-free. Towards the end, the reaction should be quickened by application of heat. The whole operation covers about half an hour.

Practically all of the sulphur is thus converted into hydrogen sulphide. There remains in the generator neither free sulphur nor sulphuric acid: very small amounts of organic sulphides will pass over unabsorbed through the absorber. Cadmium sulphide formed is then filtered, well washed, and transferred together with the filter paper into a beaker, where it is titrated with iodine and thiosulphate.

RESULTS.

Results obtained with the ordinary evolution method are generally taken as too low, being often as low as nearly half of those with the gravimetric method and also of those obtained with my modification. As already remarked some of the sulphur remains in the case of the ordinary method kept either as solid in the generator, which can be detected on being fused with alkalis and tested for sulphates, or as sulphates in solution. Furthermore, some of the sulphur is then more liable to escape as organic sulphides due to the slow action of acids. Therefore a bottle containing a solution of an alkaline permanganate and connected to the absorber always shows the presence of much greater quantities of sulphates.

In spite of these facts, i. e. that the sulphur is scattered in several places, the old method is not ready to take into account anything but the results shown in the absorber. The new method is, however, to add numbers both from the absorber and the second wash-bottle

whereas those for organic sulphides are laid aside on account of their being so trifling. The following table will show clearly these relations and the comparative efficacy of both methods :—

TABLE 1.

Pig iron	Analytical method	S in Generator		S	S	S	S	S
		as solid residue in %	in solution in %	in II. wash-bottle in %	in absorber in %	in KMnO_4 solution in %	total in %	S indicated on analysis in %
No. 1.	new	0	0	0.02	0.30	0.01	0.33	0.32
	old	0.03	0.05	0.01	0.21	0.04	0.34	0.21
No. 2.	new	0	0	0.02	0.10	0.01	0.13	0.12
	old	0.04	0.02	0.01	0.06	0.02	0.15	0.06

Experiments were then made with zinc sulphide containing 31.21%S instead of 32.85% for the pure sample, mixed with pig iron of 0.016% sulphur as determined gravimetrically, either in presence of zinc amalgam or not. The total sulphur minus that from the pig iron is compared with the theoretical number for zinc sulphide :—

TABLE 2.

Method	Mixture		S total (found)	S in pig iron	S in ZnS	S in ZnS (calc.)	S in ZnS (found)
	zinc sulphide	pig-iron w. 0.016%S	I.	II.	I-II.	(calc.)	(found)
	in gr.	in gr.	in gr.	in gr.	in gr.	in gr.	in %
Without zinc-amalgam	0.0661	3.2	0.0205	0.0005	0.0200	0.0206	97.09
	0.0628	3.2	0.0197	0.0005	0.0192	0.0196	98.47
With zinc-amalgam	0.0611	3.2	0.0194	0.0005	0.0189	0.0191	99.00
	0.0633	3.2	0.0202	0.0005	0.0197	0.0197	100.00

We see that the results are better with the use of zinc amalgam and approach nearly to the theoretical number.

Comparison should now be made of the new method with the barium sulphate method. On dissolving pig iron with conc. nitric acid, some of the sulphur will be lost in the form of hydrogen sulphide, which is therefore to be caught and added to the sulphur found as barium sulphate. These are then compared with the results of my method :—

TABLE 3.

Pig iron	Gravimetric method S in %	New evolution method S in %
No. 3.	0.36 0.42 0.42 Mean : 0.40 0.41 0.38	0.40

For the same purpose, some of the standard sample⁴ of pig iron, the Bureau of Standards, U. S. A., was analysed with the following results :—

TABLE 4.

Statements in the certificate of B. S.		New evolution method S in %
Gravimet. method S in %	Evolution method S in %	
0.049	0.038	0.05

Hence we see the new method is in all cases giving the same results as those of the gravimetric analysis.

Finally, as to the concentration of the acid, we have used that of sp. gr. 1.20 in the course of this work, but weaker acid down to sp. gr. 1.15 can safely be employed as will be seen from the following table :—

⁴ *Vide* Circular of the Bureau of Standards, No. 25, 1922, p. 7.

TABLE 5.

With acid of sp. gr. 1.20 S in %	With acid of sp. gr. 1.15 S in %	Gravimetrically determined S in %
0.11	0.10	0.11
0.11	0.10	0.12
0.11	0.10	0.12

SUMMARY.

A modification of the evolution method is intended by the use of a stronger acid, sp. gr. 1.15—1.20, in presence of zinc amalgam. The results are reliable and always in accordance with those obtained gravimetrically.

My cordial thanks are due to Prof. M. Chikashige for his thorough revision kindly undertaken for this paper.

Electrolytic Reduction of Oximes, I. Benzoinoxime

By

Masayoshi Ishibashi

(Received May 17, 1923)

Electrolytic reduction of oximes generally takes place so smoothly that some of the reaction is believed to afford the best mode of preparation for amines. As the works on this field, however, are rather few, and many points are left still untouched the author has taken up the problem to study it more thoroughly. The present communication dealing with the reduction of benzoinoxime forms the first report of the experimental works thus planned for carrying out.

Benzoinoxime (α -compound melting at 150–151°) prepared from benzoin and hydroxylamine according to the method of H. Goldschmidt and N. Polonowska¹ was used. A solution formed by dissolving 10 grams of the oxime in 100 c.c. of alcohol with 10 c.c. of a concentrated sulphuric acid added was taken as the cathode solution in a beaker, into which a porous cell filled with a dilute sulphuric acid was dipped so as to form the anode compartment. Using a lead plate of 136 sq. cm. as the cathode a current of 0.6 ampere was passed for about 8 hours, during which the temperature of the bath was maintained at 25° by cooling it with water. When the current was passed for nearly 3 hours, the evolution of hydrogen in the cathode greatly increased, and the cathode became coated with very minute crystals.

After the electrolysis was over the yellow-coloured cathode solution was poured into water and left to stand over-night, and then

¹ Ber. D. Chem. Ges., **20**, 492 (1887).

filtered. The precipitate (I) consisting of a white crystalline substance contaminated with some oily liquid was boiled with water for about 20 minutes with the object of separating the soluble part from the insoluble. The insoluble portion, when recrystallised from alcohol, formed colourless prisms melting at 135-137°, and having all the properties of benzoin; the soluble portion crystallized out from the aqueous solution in fine needles which, on further treatment with dilute alcohol, were separated into two parts, that is, the less soluble one crystallizing in plates, with the melting point at 137-138°, and the more soluble one crystallizing into fine needles, with the melting point at 119-120°. The former was proved to be hydrobenzoin, and the latter isohydrobenzoin.

The filtrate separated from the precipitate (I), after having been confirmed to contain hydroxylamine, was made alkaline by sodium hydroxide and left to stand for 12 hours. The precipitate, gradually changing from the amorphous to the crystalline, was gathered and purified by recrystallizing it from benzene. As it was deemed to be a mixture of normal and iso-diphenyloxyethylamine,¹ it was treated with benzene with the object of separating the two substances from each other, and by this process 2 grams of the normal compound (M. P. 160°) and 0.2 gram of the isocompound (M. P. 129°) were obtained. They were each analysed by Kjeldahl's method with the following results:

Substance taken gram.	$\frac{\text{N}}{20}\text{HCl}$	$\frac{\text{N}}{\text{Found}} \quad \frac{\text{N}}{\text{Calc.}(\text{C}_{14}\text{H}_{15}\text{NO})}$	
		Found	Calc.
0.4550	4.2 c.c.	6.98	6.57%
0.5010	4.6 „	7.02	

On standing the normal amine with alcoholic hydrogen chloride needle crystals² melting at 210° were produced, and that it was amine hydrochloride was confirmed by titrating it with $\frac{\text{N}}{10}$ NaOH.

¹ H. G. Söderbaum; Ber. D. Chem. Ges., **28**, 2522 (1895)

² N, Polonowska; *ibid.*, **21**, 488 (1888)

In order to test the substance crystallized out on the surface of cathode during the electrolysis, it was dissolved in hot benzene, and recrystallized from alcohol, in which it is soluble only at a high temperature. The melting point of the needle crystals thus purified was found to be 207–208°. Possibly the substance may be benzoinpinacone, but as the true melting point of benzoinpinacone¹ is not yet settled, its determination affords no reliable means for its identification. So that it was subjected to elementary analysis, and the following results were obtained.

1. 0.1010 grm. substance gave 0.3000 grm. CO₂ and 0.0590 grm. H₂O
2. 0.1248 „ „ „ 0.3760 „ „ „ 0.0770 „ „
3. 0.1234 „ „ „ 0.3763 „ „ „ 0.0778 „ „
4. 0.0984 „ „ „ 0.2880 „ „ „ 0.0607 „ „

	Found				Calc.	
	1	2	3	4	for C ₂₈ H ₂₆ O ₄	for C ₂₈ H ₂₆ O ₂
C	81.09	82.21	83.30	80.98	78.85	85.24 %
H	6.54	6.82	6.89	6.90	6.15	6.64 %

From the above results it is clearly seen that the substance used for the analysis is neither benzoinpinacone nor desoxybenzoinpinacone², but a mixture of the two.

Drawing an inference from the reduction-products thus far identified, it may be concluded that benzoinoxime undergoes electrolytic reduction in an acid solution only partly, and some part of it is hydrolysed before it is electrolytically reduced, and benzoin produced by hydrolysis undergoes reduction simultaneously so as to form hydrobenzoin, benzoinpinacone, and desoxybenzoinpinacone.

To find out the most favourable condition of electrolysis for the

¹ Melting point of benzoinpinacone given by Goldenberg [Lieb. Ann., **174**, 332 (1874)] is 208°, while Zinke [(Lieb. Ann., **198**, 52 (1879))] announced it to be 233°, and Kauffmann [Zs. Elektrochemie **4**, 461 (1898)] 235°.

² As the melting point of desoxybenzoinpinacone, 213° (α-compound) and 172° (β-compound) are given by Blank [Lieb. Ann., **248**, 1 (1888)].

production of the amine a series of experiments were conducted, the results of which are summarized in the following tables.

1. Influence of the concentration of sulphuric acid

Cathode solution :	3.0 grm benzoinoxime 100 c.c. alcohol sulphuric acid (1.83)
Anode solution :	dilute sulphuric acid
Chthode :	lead plate (136 sq. cm)
Current strength :	0.4 amperes
Time of electrolysis :	8 hours
Temperature :	7-8°

Table [I]

Conc. of H ₂ SO ₄	Benzoin	Hydro- benzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
%	grm.	grm.	grm.	grm.	%	%
5	0.36	0.08	—	1.30	20.14	46.70
10	0.22	0.01	trace	0.73	11.25	26.00
20	0.34	0.05	trace	0.70	10.81	18.17

2. Influence of current density

Cathode solution :	3.0 grm benzoinoxime 100 c.c. alcohol 10 c.c. H ₂ SO ₄ (1.83)
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Other conditions are the same as in 1.

Table [II]

Current density	Benzoin	Hydro- benzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
amp./100cm ²	grm.	grm.	grm.	grm.	%	%
0.3	0.22	0.01	trace	0.73	11.25	26.00
0.4	0.80	0.30	trace	0.65	10.25	23.60
0.5	1.12	0.38	trace	0.51	7.81	8.20

3. Influence of temperature

The conditions are the same as in 2.

Table [III]

Temperature	Benzoin	Hydrobenzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
	gram.	gram.	gram.	gram.	%	%
7- 8°	0.22	0.01	trace	0.73	11.25	26.00
19-20°	0.15	trace	little	1.31	20.16	46.78
50-52°	trace	trace	0.37	0.02	0.31	0.94

4. Influence of cathode material

Cathode solution : 3.0 gram benzoinoxime
 100 c.c. alcohol
 5 c.c. sulphuric acid (1.83)
 Anode solution : dilute sulphuric acid
 Temperature : 7-8°
 Current strength : 0.6 amperes
 Time of electrolysis : 8 hours

Table [IV]

Cathode		Benzoin	Hydrobenzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
Material	Surface area						
	sq. cm.	gram.	gram.	gram.	gram.	%	%
Pb(Amalgam)	136	0.08	trace	0.02	1.10	11.46	39.15
Pb	136	0.36	0.08	—	1.30	13.75	46.70
Sn	141	0.50	0.02	trace	1.39	14.87	49.55
Ni	66	2.55	0.10	—	trace	—	—

From the above results it may be concluded that for the preparation of the amine the concentration of sulphuric acid in the cathode solution should not exceed 5 %, and the electrolysis should be conducted at 19—20° with current density of about 0.3 amperes per sq. cm., and as cathodes tin and lead are most preferable.

In an alkaline or neutral solution, hydrolysis of the oxime does not take place, but at the same time no appreciable reduction could be observed.

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